

RESEARCH ARTICLE

A NOVEL ECO-FRIENDLY PHENOLIC RESIN MODIFIED WITH UREA/SODIUM HYDROXIDE SOLUTION-TREATED SOYBEAN MEAL

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ABSTRACT

Plant proteins are recognized for their environmental benefits, including a low carbon footprint, renewability, abundant availability, and cost-effectiveness, making them ideal raw materials for biomass-based eco-friendly adhesives. In this study, a green, environmentally friendly soybean protein-modified phenolic resin was synthesized by treating soybean meal with sodium hydroxide/urea aqueous solution. FTIR analysis results of PF and U-SMPF resins shows that the peptide chain structure of soybean protein was incorporated into the phenolic resin, undergoing co-condensation with phenol and formaldehyde to form co-condensed compounds. The 30% U-SMPF resin shows the highest bonding strength at 0.92 MPa, suggesting that the monosaccharides generated from soybean meal treated with sodium hydroxide/urea solution have a limited effect on the bonding strength of the co-condensed resin.

KEYWORDS

Environmentally, hydroxide/urea, peptide chain, monosaccharides

1. INTRODUCTION

Plant proteins are recognized for their environmental benefits, including a low carbon footprint, renewability, abundant availability, and cost-effectiveness, making them ideal raw materials for biomass-based eco-friendly adhesives (Cheng et al., 2016). In the early 20th century, protein-based adhesives were developed but were replaced by aldehyde-based adhesives due to inferior bonding performance. However, the depletion of petroleum resources and growing environmental concerns have sparked renewed interest in eco-friendly, renewable protein adhesives (Cheng et al., 2016; Cheng et al., 2017; Jin et al., 2020). Common protein sources include soybeans, peanuts, waste feathers, cottonseed, animal blood, and wheat. Soy protein, a byproduct of the soybean oil industry, is widely used in wood adhesives due to its non-toxicity, biodegradability, cost-effectiveness, and ease of processing. However, the mechanical properties and water resistance of soy protein adhesives are relatively weak, limiting their application (Kang et al., 2019; Liu et al., 2017; Song et al., 2016; Vnucec et al., 2017; Xu et al., 2020; Otto et al., 2016). To address these limitations, extensive research has focused on enhancing the performance of soy protein-based adhesives through methods such as activation, enzymatic hydrolysis, and cross-linking (Chen et al., 2017; Li et al., 2020; Pradyawong et al., 2017; Tian et al., 2018; Moubarik et al., 2009; Wang et al., 2018).

Currently, substantial research on plant protein adhesives is being conducted both domestically and internationally. However, research on modifying phenolic resins with plant proteins to reduce costs remains limited (Amirou et al., 2019; Chen et al., 2020; Liang et al., 2019; Yue et al., 2019). Phenolic resin can serve as a crosslinking agent in plant protein-based adhesives (Wu et al., 2019; Wang et al., 2017). A group of researchers investigated the bonding of high-moisture birch veneer (15%) using soy protein isolate (SPI)-modified phenolic (PF) resin (Ortynska et al., 2018). SPI enhances the bonding strength. When three mass units of SPI are added, the shear strength reaches its peak. However, an increased SPI content reduces the shear strength. The bonding performance of plywood

at 150°C is superior to that at 130°C. The modified PF resin meets the EN 314-2 external bonding quality standard and is recommended for industrial applications. A studied soy flour-modified phenolic resins and applied them to oriented strand board (OSB) (Wescott and Frihart, 2004). The soy flour was initially treated under alkaline conditions at 70°C, followed by gradual addition of formaldehyde and phenol. The final modified phenolic resin had a substitution rate of 4%. The results indicated that the oriented strand board prepared with this modified phenolic resin exhibited properties similar to those of pure phenolic resin.

Furthermore, the modified resin produced by this method exhibited excellent storage stability, environmental friendliness, and low costs. A group of researchers modified phenolic resins with soy flour to prepare copolymer resins (Yang et al., 2006). One method involved cross-linking soy flour with phenolic resin under neutral conditions, while another method involved hydrolyzing soy flour followed by copolymerization of the hydrolysis products with phenolic resin under alkaline catalytic conditions. The modified resin (APS), synthesized under alkaline conditions, was mixed with a small amount of corn flour to produce plywood with good water resistance, suitable for outdoor use. A group of researchers further investigated the liquefaction of soy flour under alkaline conditions, followed by blending with urea-formaldehyde and phenolic resins to prepare medium-density fiberboard (Yang et al., 2006). When soy protein was blended with phenolic resin, the resulting medium-density fiberboard exhibited good performance. Moreover, the medium-density fiberboard prepared by blending with phenolic resin exhibited excellent boiling water resistance, making it suitable for outdoor use.

Plywood made with phenolic resin modified by soy protein isolate at a high substitution rate demonstrates excellent mechanical strength. However, the high cost of soy protein isolate increases the production costs of SPF resin. To further reduce costs, this study uses soybean meal, a more cost-effective alternative to soy protein isolate. Furthermore, the soybean meal is liquefied with a sodium hydroxide/urea aqueous solution and used to modify phenolic resin, resulting in the production of a new, environmentally friendly U-SMPF resin. The chemical structure and

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properties of the modified resin were characterized and analyzed using FTIR, TG, DSC, and various physical and chemical property tests.

2. MATERIALS AND METHODS

2.1 Materials

The formaldehyde solution (37.4% analytical grade) and phenol (98% analytical grade) were supplied by Xilong Scientific Co., Ltd., Shantou, Guangdong Province. Urea (98% industrial grade) was obtained from PetroChina Ningxia Petrochemical Company. Sodium hydroxide (analytical grade) was sourced from Beijing Chemical Plant. Soybean meal (43% protein content, industrial grade) was purchased from Shandong Xiangchi Grain and Oil Co., Ltd.

2.2 Methods

2.2.1 Treatment of Soybean Meal with Sodium Hydroxide/Urea Aqueous Solution

Prepare the solution using urea, sodium hydroxide, and water in a ratio of 12:7:21 by weight. Soybean meal was gradually added to the sodium hydroxide/urea aqueous solution under magnetic stirring, with the mass of the soybean meal constituting 40% of the solution's mass. After being treated in a water bath at 60°C for 30 minutes, the mixture was cooled to room temperature and stirred for 4 hours. Stirring was then stopped, and the mixture was left to stand for further use.

2.2.2 Synthesis of the Phenolic Resin

One hundred grams of molten phenol (P), distilled water, and a portion of 40% NaOH solution were added to a four-necked flask. After stirring for 5 minutes at 50°C, the first batch of formaldehyde was introduced. The temperature was then gradually raised to 90°C in a water bath over 20–25 minutes. The reaction was allowed to proceed at 90°C for 40 minutes, after which the second batch of formaldehyde and NaOH solution was added. The reaction continued at 90°C for 30 minutes, followed by the addition of the third batch of formaldehyde. The reaction was maintained at 90°C for an additional 30 minutes, after which the mixture was rapidly cooled to 40°C and discharged, yielding pure phenolic resin (PF) with a molar ratio of F/P = 2.2.

2.2.3 Synthesis of Phenolic Resin Modified with Soybean Meal

A specified amount of molten phenol, distilled water, catalyst, soybean meal liquefaction product, and a portion of 40% NaOH solution were added to a four-necked flask. After stirring for 5 minutes at 50°C, the first batch of formaldehyde was introduced. The temperature was gradually raised to 90°C in a water bath over 20 to 25 minutes. The reaction proceeded at 90°C for 30 minutes, after which the remaining soybean meal liquefaction product, second batch of formaldehyde, and sodium hydroxide were added. The reaction continued at 90°C for 30 minutes, followed by the addition of the third batch of formaldehyde. The reaction was maintained for an additional 30 minutes, then the mixture was rapidly cooled to 40°C and discharged, yielding the sodium hydroxide/urea-treated soybean meal co-condensation modified phenolic resin (U-SMPF). The mass ratio of U-SM to (P+F) was 0.1 to 0.4. In this study, U-SMPF resins with substitution rates ranging from 10% to 40% were synthesized.

2.3 Physical and Chemical Property Testing of Resins

The basic physicochemical properties of PF resin and 10% to 40% U-SMPF

resin, including pH, viscosity, solid content, and gel time, were tested according to the "Test Methods for Wood Adhesives and Their Resins" (GB/T 12074-2013).

2.4 Structural Characterization and Thermal Analysis of Resins

Samples of soybean meal (SM), liquefied soybean meal (U-SM), phenolic resin (PF), and liquefied soybean meal-modified phenolic resin (U-SMPF) were freeze-dried. The dried samples were ground into 200-mesh powder (Li et al., 2016). The samples were analyzed using the tablet method with the following parameters: scanning range from 4000 to 400 cm^{-1} , resolution of 4 cm^{-1} , and 32 scans. Samples were placed at 120°C for 2 hours to ensure complete curing and drying. The samples were ground into 200-mesh powder and analyzed using the TA Q50 thermal analyzer (American TA). A 5 mg sample was placed in a platinum pan, with the following experimental parameters: N_2 protection, heating rate of 10°C/min, and a temperature range from room temperature to 650°C.

2.5 Plywood Preparation and Performance Evaluation

The bonding performance and formaldehyde emission of PF and U-SMPF resins were assessed using three-layer poplar plywood prepared by hot pressing. To increase the resin viscosity, 15% flour was added as a filler, and the mixture was uniformly stirred using high-speed mechanical agitation. The adhesive was manually applied to the upper and lower veneers, with the core veneer placed perpendicular to the surface veneer grain direction. The adhesive application rate was 160 g/m^2 . The hot pressing parameters were as follows: pressing temperature was 135°C, pressing time was 360 s, and the pressing pressure was 1.2 MPa. The prepared plywood was placed in an indoor environment to equilibrate its moisture content, and after one week, its mechanical properties and formaldehyde emission were measured. The bonding strength and formaldehyde emission of plywood prepared with phenolic resin and modified resin were determined following the relevant standard methods in the national standard "Test Methods for Physical and Chemical Properties of Wood-based Panels and Surface Decorated Wood-based Panels" (GB/T 17657-2013). The bonding strength was tested following the relevant standard methods for Class I plywood.

3. RESULTS AND DISCUSSION

3.1 FTIR Analysis of Different U-SMPF Resins

Figure 1 presents the infrared spectra of phenolic resins modified with soybean meal treated with various concentrations of sodium hydroxide/urea aqueous solution. The absorption peaks at 1607 cm^{-1} and 1487 cm^{-1} correspond to the characteristic C=C stretching vibrations of the benzene ring in the phenolic resin (Chen et al., 2020; Gu et al., 2020). Compared to the PF resin spectrum, the U-SMPF resin displays a new absorption peak at 1668 cm^{-1} , indicative of the amide I structure in proteins. This suggests that peptide bonds were incorporated into the PF resin, with soy protein isolate undergoing a co-condensation reaction with phenol and formaldehyde, resulting in a uniform co-condensation compound structure. A new absorption peak at 1367 cm^{-1} arises from the transformation of protein COO⁻ in soybean meal to the O=C-OR structure (Lei et al., 2016). These changes in absorption peaks suggest that the sodium hydroxide/urea-treated soybean meal underwent a co-condensation reaction with phenol and formaldehyde, forming a co-condensation compound (Li et al., 2014).

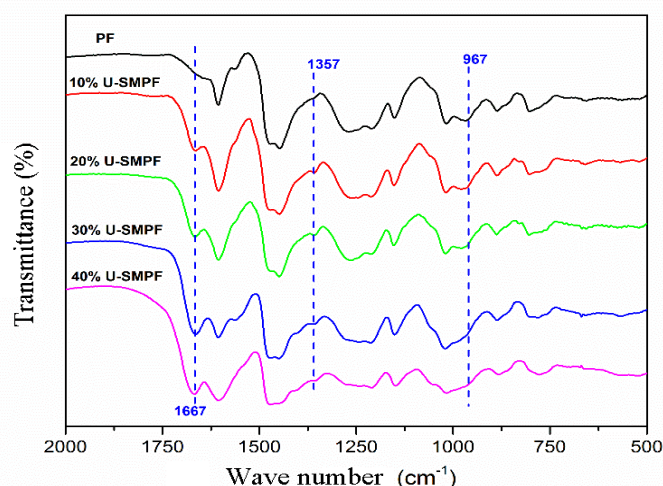


Figure 1: FTIR spectra of different U-SMPF resins

3.2 DSC Analysis of U-SMPF Resins

Figure 2 displays the DSC curves of U-SMPF resins with varying substitution levels. As shown in Figure 2, both PF resin and 10% to 30% U-SMPF resins exhibit a single exothermic peak, whereas the 40% U-SMPF resin shows two exothermic peaks. The peak temperature of the 30% U-SMPF resin is slightly lower (134.57°C) compared to that of the PF resin, while the peak temperatures of the other U-SMPF resins are higher than the PF resin and increase with the substitution level of liquefied soybean

meal. The 40% U-SMPF resin exhibits two exothermic peaks, with the first at 141.21°C and the second at 152.91°C. At a 40% substitution level, the soybean meal treated with sodium hydroxide/urea aqueous solution contains a significant amount of urea, which undergoes a co-condensation reaction with phenol and formaldehyde under the experimental conditions, leading to a higher curing temperature for the copolymer. This suggests that the curing temperature of phenolic resin modified by co-condensation with sodium hydroxide/urea-treated soybean meal is higher than that of the PF resin.

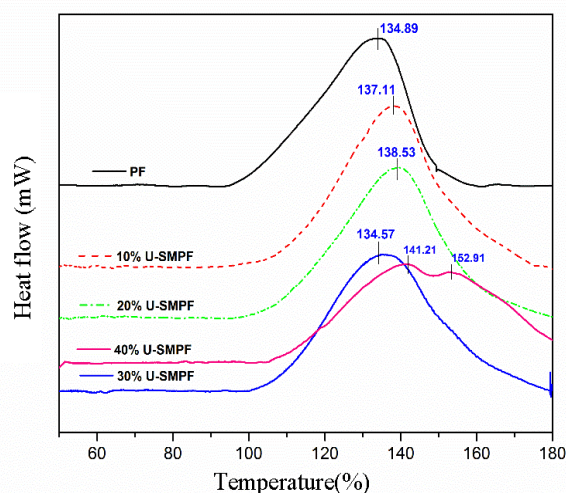


Figure 2: DSC curves of different U-SMPF resins

3.3 Analysis of TG and DTG of U-SMPF Resin

Figure 3 presents the TG and DTG curves of U-SMPF resins with varying substitution levels. As shown in Figure 3 and Table 1, the total weight loss rate of U-SMPF resins increases as the substitution level of sodium hydroxide/urea-treated soybean meal rises. The total weight loss rates for 10% to 40% U-SMPF resins in the 30°C to 650°C range are 33.89%, 37.73%, 42.71%, and 45.66%, respectively, all exceeding that of the PF resin. This indicates that the thermal stability of phenolic resin modified with sodium hydroxide/urea-treated soybean meal is lower than that of pure phenolic resin. In the first stage of resin pyrolysis, the weight loss peaks for SMPF resins with 10% and 20% substitution levels each show two peaks, with the second peak temperature higher than that of the PF resin. The SMPF resins with 30% and 40% substitution levels each show one TP2 weight loss peak, with peak temperatures lower than those of the 10% and 20% resins.

Additionally, the weight loss rate of the U-SMPF resins increases with the substitution level of sodium hydroxide/urea-treated soybean meal. In the second stage, the 10% SMPF resin exhibits the smallest weight loss rate, whereas the 20% SMPF resin shows the largest weight loss rate and the lowest peak temperature. In the third stage, the 10% SMPF resin has the smallest weight loss rate, while the 20% SMPF resin has the largest. Overall, the data suggest that different substitution levels of soybean meal significantly affect the thermal stability of the modified phenolic resin and influence its chemical structure and curing. In the first stage of pyrolysis, the 20% SMPF resin exhibits the best thermal stability. Throughout the pyrolysis stage, the 40% SMPF resin shows the poorest thermal stability. Data analysis reveals that the thermal stability of U-SMPF resins with varying substitution rates is lower than that of pure phenolic resin. Notably, as the U-SM substitution proportion for phenol increases, the thermal stability of the U-SMPF resin continues to decrease. This is because U-SM, a biomass material, has lower pyrolysis stability.

Table 1: Thermal properties of the cured U-SMPF resins

Adhesive	The first stage 100-310 °C			The second stage 310-430 °C		The third stage 430-550 °C		Total weight loss %
	T _{P1} (°C)	T _{P2} (°C)	Weight loss %	T _{P3} (°C)	Weight loss %	T _{P4} (°C)	Weight loss %	
PF	-	-	245	7.89	378	9.05	494	
10% U-SMPF	208	-	287	10.32	394	8.81	486	
20% U-SMPF	187	-	261	13.14	390	10.53	479	
30% U-SMPF	-	-	249	15.23	388	13.18	481	
40% U-SMPF	-	-	251	16.36	381	15.71	471	

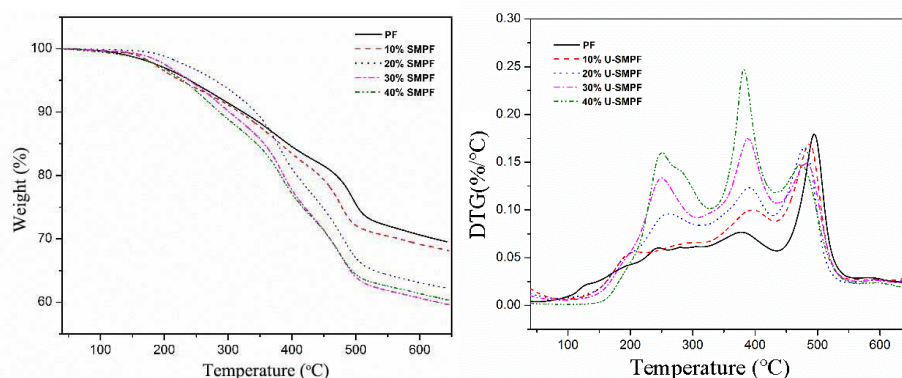


Figure 3: TG and DTG curves of different U-SMPF resins

3.4 Analysis of Physicochemical Properties of U-SMPF Resins

Table 2 presents the physicochemical properties of U-SMPF resins with varying substitution levels. Table 2 shows that the pH values of U-SMPF resins with varying substitution levels range from 12.28 to 12.73, while the solid content of the modified resins is maintained between 39% and 40%. As the substitution level of sodium hydroxide/urea-treated soybean meal increases, the viscosity of U-SMPF resins also increases. Additionally, the gel time of U-SMPF resins decreases with higher substitution levels, and their storage period exceeds 30 days. At higher substitution levels, the soybean protein molecules in sodium hydroxide/urea-treated soybean meal unfold and partially degrade, exposing a significant number of amino

groups (Chang et al., 2020). Simultaneously, some polysaccharides dissolve in the sodium hydroxide/urea solution and partially degrade (Wu et al., 2020). Although the 40% U-SMPF resin exhibits a high viscosity of 1027 mPa·s at 25°C, experiments showed that increasing the temperature to 40°C and stirring causes the viscosity to drop sharply, making the resin easier to apply. Compared to pure phenolic resin, U-SMPF resin has a shorter gel time, related to its higher viscosity. The molecular weight of U-SMPF resin is greater than that of pure phenolic resin, and its gel time is shorter. As the U-SM substitution level increases, the viscosity of U-SMPF resin gradually decreases. Additionally, the gel time of U-SMPF resin decreases with higher U-SM substitution levels.

Table 2: Characteristics of U-SMPF resins

Name of resin	pH	viscosity (mPa·s)	Solid content (%)	Gel time (s)	Storage period (d)
Control PF	12.11	100	43.87	552	>30
PF	11.98	87	43.85	571	>30
10% U-SMPF	12.73	94	39.24	467	>30
20% U-SMPF	12.31	213	39.80	443	>30
30% U-SMPF	12.28	517	39.60	405	>30
40% U-SMPF	12.38	1027	39.71	351	>30

3.5 Bonding Strength and Formaldehyde Emission

Figure 4 presents the bonding strength and formaldehyde emission of PF resin and U-SMPF resins with varying substitution levels. As shown in Figure 4, the bonding strengths of 10–40% U-SMPF resins are 0.77, 0.77, 0.92, and 0.85 MPa, respectively, all lower than those of the control PF resin and standard PF resin. However, all of them meet the national standard requirements for Class I plywood adhesive strength. The bonding strength of U-SMPF resins decreases compared to PF resin, indicating that treating soybean meal with sodium hydroxide/urea solution does not improve the bonding performance of modified phenolic resins. The main components of the treatment solution, urea and sodium hydroxide, degrade protein carbon chains and polysaccharides in soybean meal, reducing molecular weight and converting polysaccharides into monosaccharides, which lowers the water resistance of the co-condensed resin (Li et al., 2016; Li et al., 2018). Thus, the overall bonding strength of U-SMPF resins is lower than that of SMPF resins. Among these, the 30% U-SMPF resin shows the highest bonding strength at 0.92 MPa, suggesting

that the monosaccharides generated from soybean meal treated with sodium hydroxide/urea solution have a limited effect on the bonding strength of the co-condensed resin. The main structure of U-SMPF resin is formed by co-condensation between the protein peptide chains in soybean meal and phenol and formaldehyde, allowing the modified resin to meet the Class I plywood bonding strength requirements. Figure 4 also shows that as the substitution level of sodium hydroxide/urea-treated soybean meal increases, the formaldehyde emission of U-SMPF resins first decreases, then increases, and decreases again. The formaldehyde emissions of the modified resins are 0.53, 0.53, 1.06, and 0.97 mg/L, respectively, all of which exceed the E0 grade plywood standard for formaldehyde emission (0.5 mg/L). The formaldehyde emissions of 10% and 20% U-SMPF resins are lower than that of PF resin, whereas those of 30% and 40% U-SMPF resins exceed that of PF resin. Overall, the bonding strength of U-SMPF resins is lower than that of phenolic resin; however, at lower substitution levels, treating soybean meal with sodium hydroxide/urea solution reduces the formaldehyde emission of the modified resin.

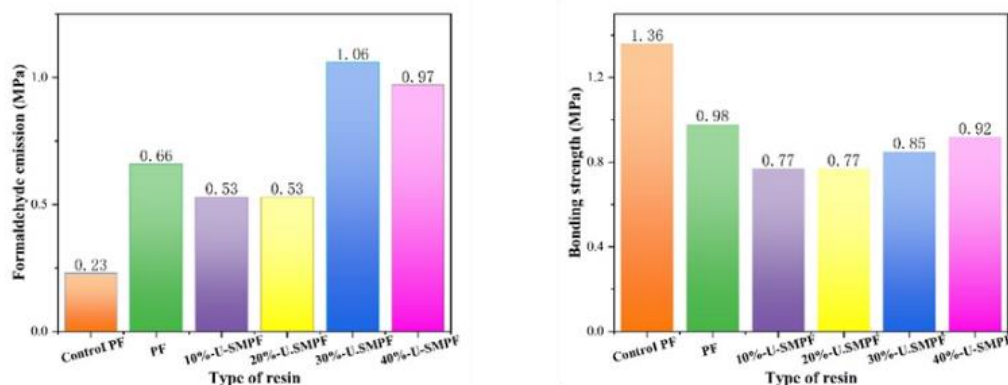


Figure 4: The bonding strength and formaldehyde emission of different U-SMPF resins

4. CONCLUSION

In this study, a green, environmentally friendly soybean protein-modified phenolic resin was synthesized by treating soybean meal with sodium hydroxide/urea aqueous solution. The results show that the chemical structure of soybean meal was significantly altered, with the protein's molecular structure disrupted and degraded. Comparative FTIR analysis of PF and U-SMPF resins shows that the peptide chain structure of soybean protein was incorporated into the phenolic resin, undergoing co-condensation with phenol and formaldehyde to form co-condensed compounds. For U-SMPF resin, as the U-SPI substitution level increases, the peak temperature of the curing exothermic peak rises and remains consistently higher than that of PF resin. Treating soybean meal with sodium hydroxide/urea aqueous solution improves its thermal stability. However, the thermal stability of the co-condensed modified phenolic resin from soybean meal is lower than that of pure phenolic resin. The

thermal stability of co-condensed modified phenolic resin from sodium hydroxide/urea-treated soybean meal is lower than that of phenolic resin, and as the U-SM substitution level increases, the thermal stability of U-SMPF resin decreases gradually. Compared to PF resin, U-SMPF resin has a shorter gel time and higher viscosity. Furthermore, U-SMPF resin meets the national standard requirements for Class I plywood adhesive strength.

AUTHOR CONTRIBUTIONS

CrediT authorship contribution statement: Conceptualization, C.L., H.L., C.W., and M.Y.; methodology, L.G.; validation, F.W. and H.L.; formal analysis, C.L. and H.L.; investigation, C.L., M.Y. and H.L.; data curation, F.Z.; writing—original draft preparation, H.L., and C.L.; writing—review and editing, C.L. and H.L.; supervision, M.Y. and H.L.; project administration, C.W., M. Y., and H.L.; funding acquisition, C.L., C.W., and H.L. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement

Not applicable.

CONFLICTS OF INTEREST

The authors declare no conflict of interest

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